

**Pyrolysis/gas chromatography/mass spectroscopy
analysis of Li-ion cell anode**

Takeshi Sasaki, Minoru Inaba, Takeshi Abe, and
Zempachi Ogumi

Department of Energy and Hydrocarbon Chemistry,
Graduate School of Engineering, Kyoto University, Sakyo-
ku, Kyoto 606-8501, Japan

Introduction

The mechanism for degradation of rechargeable Li-ion batteries has been extensively studied by many researchers. For example, irreversible lithium loss at anodes,¹ deterioration of nonaqueous electrolyte,² and an increase in the interfacial impedance at cathode³ have been considered to be responsible for the degradation. Here, we investigated by-product formation on carbonaceous anode in Li-ion cell using pyrolysis /gas chromatography/mass spectroscopy (Pyro/GC/MS) analysis technique.⁴ This analysis provides the information of relatively high-molecular-weight compounds formed on Li-ion cell anode.

Experimental

Test cells were composed of artificial graphite anode (negative electrode) and LiCoO₂ cathode (positive electrode). The anodes were prepared from graphite powder (TIMCAL G&T, SFG6, SFG15 and SFG44) mixed with PVDF. The characteristics of the graphite powder used in this study are listed in Table 1. The cathode was a mixture of LiCoO₂ powder, PVDF and conductive carbon. Prismatic cells were assembled with the anode, the cathode, a porous polyolefin separator, and electrolyte (1M LiPF₆ dissolved in EC:DEC). After being measured the initial capacities, the test cells were charged and stored at different temperatures for given periods. The cells were then disassembled, and the anodes were analyzed by Pyro/GC/MS as described elsewhere.⁴ The pyrolyzer was heated at 200°C.

Results and discussion

Figure 1 shows a typical gas chromatogram of decomposed products on anode. In addition to peaks assigned to electrolyte components (phosphoryl fluoride, DEC and EC), several additional peaks were observed at relatively high retention times. From MS analysis, peak A was identified as diethyl-2,5-dioxahexane carboxylate (DEDOHC),⁵ and peak B as an oligomer that consists of oxyethylene units.⁴ The relative intensities of peak A (DEDOHC) and peak B (an olygomer with oxyethylene units) to the EC peak are summarized in Table 2. The intensity of DEDOHC was approximately constant, and did not depend on storage period, storage temperature, and the size of graphite powder. Even on the cathode, nearly the same amounts of DEDOHC were detected. Hence it is reasonable to think that DEDOHC is a product that is soluble in the electrolyte solution. On the other hand, the intensity of the oligomer with oxyethylene units increased with increasing storage period, temperature and the BET surface area of graphite powder. The oligomer was also detected on the cathodes, however, the intensity was much lower than that on the anodes and did not depend on storage time. Therefore, the oligomer is less soluble than DEDOHC, and is a constituent of the surface film on the anodes. The observed increase of the oligomer suggests that the surface film grew during storage, especially at elevated temperatures, which results in the degradation of Li-ion batteries.

References

1. M. Broussely, S. Herreyre, P. Biensan, P. Kasztejna, K. Nechev, and R.J. Staniewicz, Extended Abstracts of the 10th IMLB, Abs. No. 3 (2000).
2. S. Sloop, J. Pugh, and J. Kerr, Extended Abstracts of the 10th IMLB, Abs. No. 188 (2000).
3. D. Zhang, B.S. Haran, A. Durairajan, R.E. White, Y. Podrazhansky, and B.N. Popov, *J. Power Sources*, **91**, 122 (2000).
4. Z. Ogumi, A. Sano, M. Inaba, and T. Abe, Extended Abstracts of the 10th IMLB, Abs. No. 148 (2000).
5. H. Yoshida, T. Fukunaga, T. Hazama, M. Terasaki, M. Mizutani, and M. Yamachi, *J. Power Sources*, **68**, 311 (1997).

Table 1 Powder characteristics of graphite.

	BET surface area / m ² g ⁻¹	D ₅₀ / um
SFG6	13	3.6
SFG15	6.6	9.4
SFG44	3.8	31

Table 2 Relative peak intensities of DEDOHC and an oligomer with oxyethylene units to EC on anode and cathode.

Anode graphite	Storage temp. / °C	Period / week	Analyzed sample	Relative peak intensity		
				EC	DEDOHC	Oligo.
SFG6	25	0	anode	100	170	13
SFG15	25	0	anode	100	160	11
SFG44	25	0	anode	100	165	10
SFG6	45	12	anode	100	150	32
SFG15	45	12	anode	100	160	20
SFG44	45	12	anode	100	150	11
SFG44	25	12	anode	100	160	8
SFG44	60	12	anode	100	150	13
SFG6	25	0	cathode	100	150	6
SFG6	45	12	cathode	100	160	6

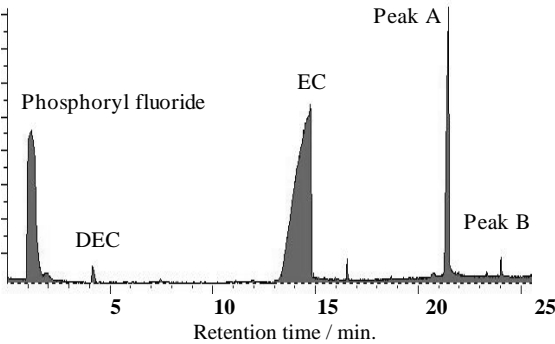


Fig.1 Gas chromatogram of thermally decomposed products on anode after storage at the charged state.